JOURNAL OF APPLIED ELECTROCHEMISTRY **21** (1991) 170–174

Influence of potassium sodium tartrate on the initial stage of silver electrodeposition

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Received 10 May 1990; revised 26 June 1990

The nucleation and growth of silver from dilute aqueous solutions of $AgNO_3$ was studied in the absence and in the presence of potassium sodium tartrate in the electrolyte. In both cases data were obtained for the rate of nucleation and growth of silver crystals at constant overpotential.

1. Introduction

Many organic substances are used as additives to electrochemical baths for industrial metal plating. Some of these are brightening or levelling agents whereas others are known to prevent dendritic growth or to improve certain physical and/or mechanical properties of the compact coatings.

An important additive to electrolytes for silver and silver alloy plating is potassium sodium tartrate ($KNaC_4H_4O_6$) [1–4]. It is the aim of the present study to demonstrate the influence of this compound on the growth and nucleation kinetics of silver from aqueous $AgNO_3$ solutions.

2. Experimental details

The growth of single silver crystals was studied in an aqueous solution of 0.05 M $AgNO_3$ + 2 M KNO_3 of pH = 1 obtained by adding HNO_3. In the studies of the nucleation kinetics the electrolyte was 0.01 M $AgNO_3$ + 1 M KNO_3 with the same value of pH. In both cases the temperature was 308 K. The working electrode was a platinum single crystal with a surface area $S_{el} = 1.4 \times 10^{-3}\,cm^2$ and bulk silver was used as counter electrode and reference electrode. The effect of two different concentrations (2.4×10^{-5} M and 4.8×10^{-5} M) of potassium sodium tartrate was investigated.

3. Growth kinetics of single silver crystals

For these studies the working electrode was polarized by means of the double pulse potentiostatic method described in detail in [5]. The overpotential and time of the first pulse were selected to form only one silver crystal on the electrode surface. During the second pulse this crystal was grown at a lower overpotential and its linear size was measured using an optical microscope at a magnification of 100. Since in all cases the silver crystals had an almost hemispherical form, all considerations in this paper are in terms of the radius, r, of the hemisphere.

Under pure diffusion control of the growth process the radius, r, of a hemispherical cluster changes with time, t, according to the equation:

$$r^2 = r_0^2 + k(t - t_0) \qquad (1)$$

where r_0 is the cluster radius at the initial moment t_0 and the growth constant, k, is given by:

$$k = 2DC_0v_m - 2DC_0v_m \exp\left[-zF\eta_g/RT\right] \qquad (2)$$

where D and C_0 are the diffusion coefficient and the bulk concentration of silver ions respectively, v_m is the molar volume of silver, η_g is the growth overpotential and all other symbols have their usual meaning.

Data for r obtained at six overpotentials in the absence of $KNaC_4H_4O_6$ are plotted against time according to Equation 1 in Fig. 1. In Fig. 2 (circles) the corresponding growth constants $k = d(r^2 - r_0^2)/d(t - t_0)$ are plotted as a function of the overpotential, η_g, according to Equation 2. The value of the diffusion coefficient, D, calculated from the k against $\exp[-zF\eta_g/RT]$ relationship is $1.86 \times 10^{-5}\,cm^2\,s^{-1}$.

The subdiagram in Fig. 1 clearly demonstrates the inhibiting effect of $KNaC_4H_4O_6$ during the growth of silver crystals. The overpotential dependence of the rate constants k obtained in the same way, but in the presence of potassium sodium tartrate, is shown in Fig. 2 by triangles ($C^* = 2.4 \times 10^{-5}$ M $KNaC_4H_4O_6$) and squares ($C^* = 4.8 \times 10^{-5}$ M $KNaC_4H_4O_6$).

In principle $KNaC_4H_4O_6$ may influence the growth process in two different ways: by decreasing the silver ion mobility if a complex of some kind is formed or by decreasing the active growing silver area if $KNaC_4H_4O_6$ is adsorbed on, or incorporated into, the silver crystals. Both effects have been experimentally registered during the growth of polycrystalline silver deposits in the presence of tartaric acid [4, 6] and it is not surprising that sodium potassium tartrate may produce similar behaviour.

Since in our case the growth law (Equation 1) does not change in the presence of $KNaC_4H_4O_6$ the two effects mentioned above can be taken into account by including a dimensionless coefficient smaller than unity in Equation 2. Thus the influence of the sodium potassium tartrate can be formally expressed in terms of an effectively lower diffusion coefficient D^*.

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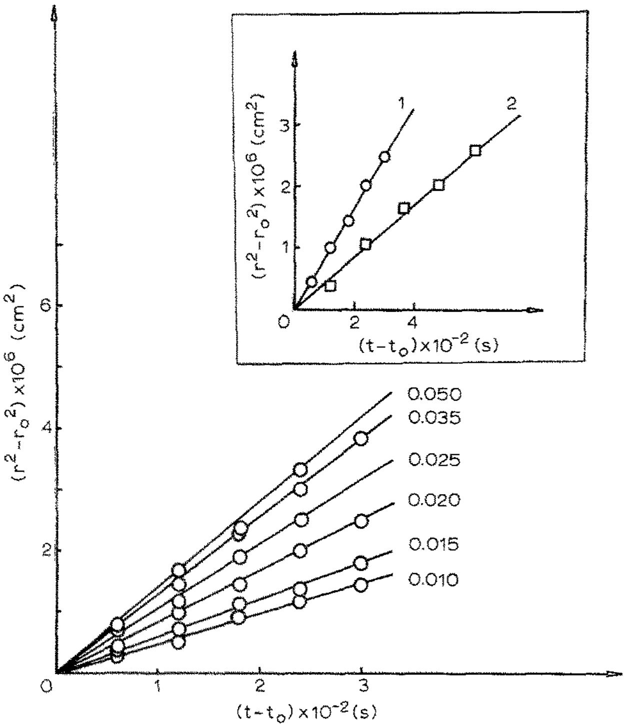

Fig. 1. Dependence of the radius r of the silver crystals on time at different growth overpotentials η_g (V). Inset: (1) in the absence and (2) in the presence of 4.8×10^{-5} M $KNaC_4H_4O_6$, $\eta_g = 0.020$ V.

The values obtained for D^* from the k against $\exp[-zF\eta_g/RT]$ relationships (Fig. 2) are $D^* = 1.70 \times 10^{-5}\,cm^2\,s^{-1}$ for $C^* = 2.4 \times 10^{-5}$ M and $D^* = 1.53 \times 10^{-5}\,cm^2\,s^{-1}$ for $C^* = 4.8 \times 10^{-5}$ M $KNaC_4H_4O_6$. Note that both D and D^* are calculated as an average of the values obtained from the slope and from the intercept of the corresponding straight lines in (Fig. 2).

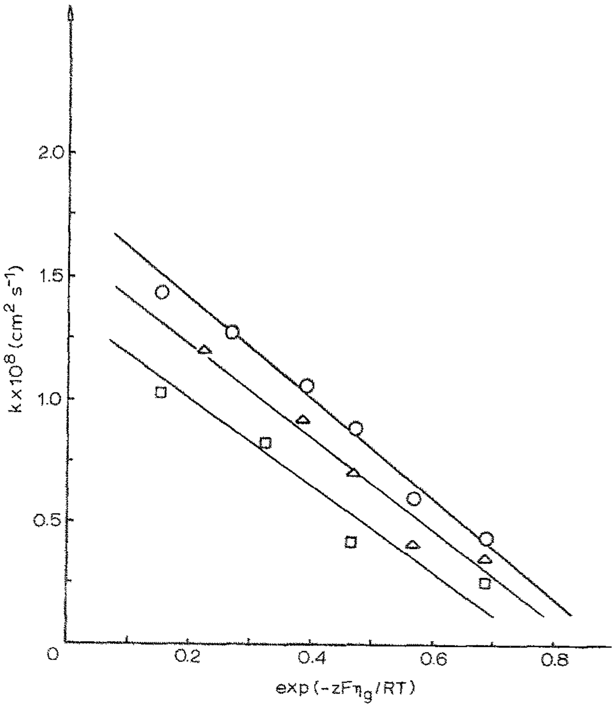

Fig. 2. Dependence of the rate constant k on the growth overpotential η_g according to Equation 2. (○) $C^* = 0$ M, (△) $C^* = 2.4 \times 10^{-5}$ M and (□) $C^* = 4.8 \times 10^{-5}$ M $KNaC_4H_4O_6$.

4. Nucleation kinetics

The nucleation kinetics of silver were studied by measuring potentiostatic current transients in the absence (Fig. 3a) and in the presence (Fig. 3b) of $KNaC_4H_4O_6$.

The experimental data for $i(t)$ were interpreted on the basis of the theoretical model of Scharifker and Mostany [7] (see also [8]) allowing an approximate, but quite simple, way of evaluating the nucleation rate constant, A, and the number, N_0, of active sites on the substrate. According to this model the values of A and N_0 can be obtained by solving numerically the equations:

$$I_m - (a/t_m)^{1/2}\{1 - \exp[-x + \alpha(1 - e^{-x/\alpha})]\} = 0 \tag{3}$$

$$\ln[1 + 2x(1 - e^{-x/\alpha})] - x + \alpha(1 - e^{-x/\alpha}) = 0 \tag{4}$$

where $I_m = i_m/S_{el}$ is the current density corresponding to the maximum of the potentiostatic transient, t_m is the time coordinate of i_m, $a = zFC_0(D/\pi)^{1/2}$, $x = N_0\pi^{3/2}D\,(8C_0v_m)^{1/2}t_m$ and $\alpha = x/At_m$. The data for A and N_0 obtained in this way are shown as functions of the nucleation overpotential, η_n, in Figs 4 and 5, respectively. As is seen the sodium potassium

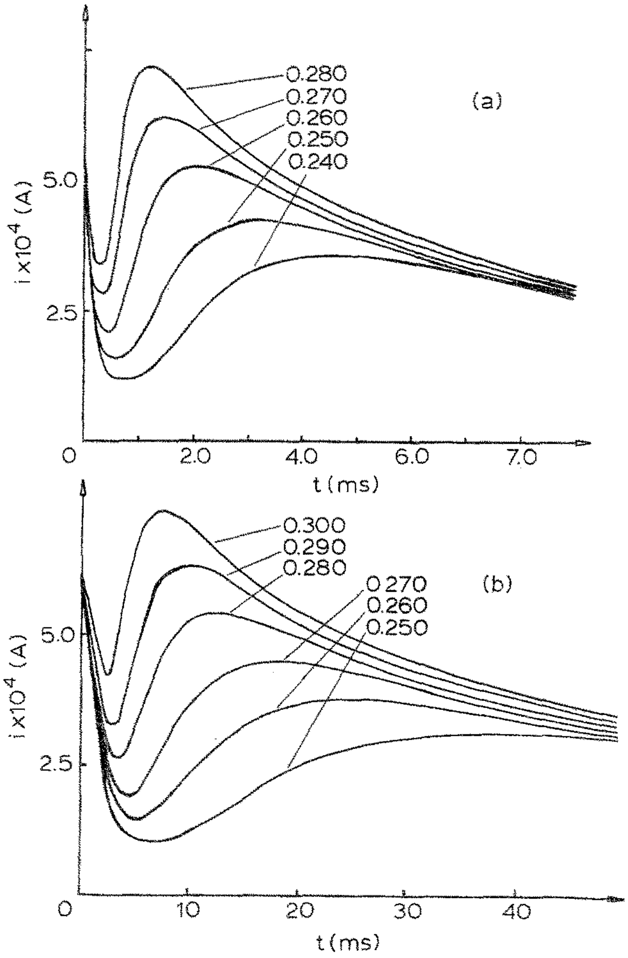

Fig. 3. Progressive current transients obtained at different nucleation overpotentials η_n (V). (a) $C^* = 0$ M, (b) $C^* = 4.8 \times 10^{-5}$ M $KNaC_4H_4O_6$.

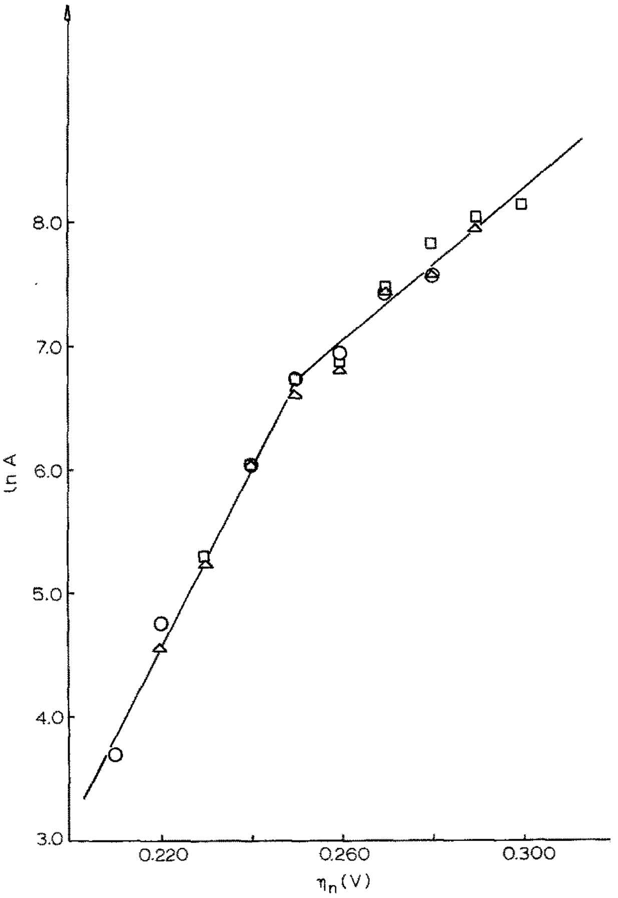

Fig. 4. Overpotential (η_n) dependence of the nucleation rate constant (A). Symbols (○, △, □) as in Fig. 2.

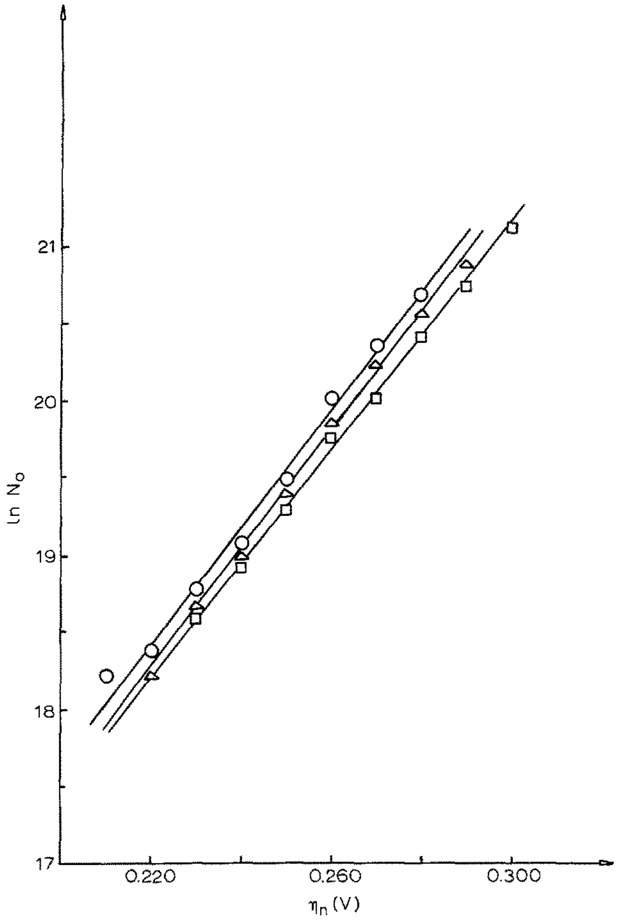

Fig. 5. Overpotential (η_n) dependence of the number of active sites (N_0). Symbols (○, △, □) as in Fig. 2.

tartrate does not affect the nucleation rate constant, A, but blocks some of the active sites for nucleation on the electrode surface. This means that the overall decrease of the current, i, in the presence of $KNaC_4H_4O_6$ (*cf.* Figs 3a and 3b) is due, not only to the decrease of the growth rate of the separate crystallites, but also to the decrease of the steady state nucleation rate $I_{st} = AN_0$. Concerning the size n_K of the critical nucleus [8, 9]

$$n_K = \frac{RT}{zF}(\mathrm{d}\ln A/\mathrm{d}\eta_n) - \beta \qquad (5)$$

From the slope of the straight line portions of the ln A against η_n relationships (Fig. 4) one obtains $n_K = 1$ atom in the overpotential interval 0.210–0.250 V and $n_K = 0$ atoms in the overpotential interval 0.250–0.300 V. Such low values for n_K are typical for the high overpotentials used in this experiment [5, 9–12]. In particular the result $n_K = 1$ means that at $\eta_n =$ 0.210–0.250 V two silver atoms form a stable cluster whereas $n_K = 0$ means that for $\eta_n > 0.250$ V the metal deposition proceeds without a thermodynamic barrier and depends only on kinetic factors. As for the number of active sites, N_0, this appears to be much lower than the atomic density of the substrate ($\sim 10^{15}\,\mathrm{cm}^{-2}$), and varies from $8.1 \times 10^7\,\mathrm{cm}^{-2}$ for $\eta_n = 0.210$ V, $C^* = 0$ M to $1.5 \times 10^9\,\mathrm{cm}^{-2}$ for $\eta_n = 0.300$ V, $C^* = 4.8 \times 10^{-5}$ M.

An exponential $N_0(\eta_n)$ relationship (Fig. 5) was found as in the case of nucleation of mercury on a platinum single crystal electrode [8].

Finally, Fig. 6 demonstrates a semiquantitative test of the applicability of the Scharifker model [7] to our experiment. The circles and triangles in this figure represent experimental data for the current density, I, obtained at $\eta_n = 0.270$ V in the absence and in the presence of $KNaC_4H_4O_6$, respectively. The lines are drawn on the basis of the theoretical formula:

$$\left(\frac{I}{I_m}\right)^2 = \frac{t_m}{t}\,\frac{\{1 - \exp[-xt/t_m + \alpha(1 - e^{-xt/t_m})]\}^2}{\{1 - \exp[-x + \alpha(1 - e^{-x/\alpha})]\}^2} \qquad (6)$$

following from the model developed in [7]. Lines a and c correspond to 'instantaneous' and 'progressive' nucleation on a substrate with a sufficiently high number of active sites ($\alpha \to 0$, $x \approx 1.26$ and $\alpha \to \infty$, $x \approx 2.34$, respectively) whereas line b represents the general case of progressive nucleation with a limited number of active sites and is drawn with $\alpha = 1.258$ and $x = 3.05$ As is seen the general formula, Equation 6, describes the whole current transients well, although α and x are derived from the coordinates (i_m, t_m) of the single points of the corresponding current maxima by solving Equations 3 and 4. (The circles and triangles in Fig. 6 represent the values of i after the initial, falling parts of the corresponding current transients, $t > 5 \times 10^{-4}$ s and $t > 6 \times 10^{-4}$ s, respectively.)

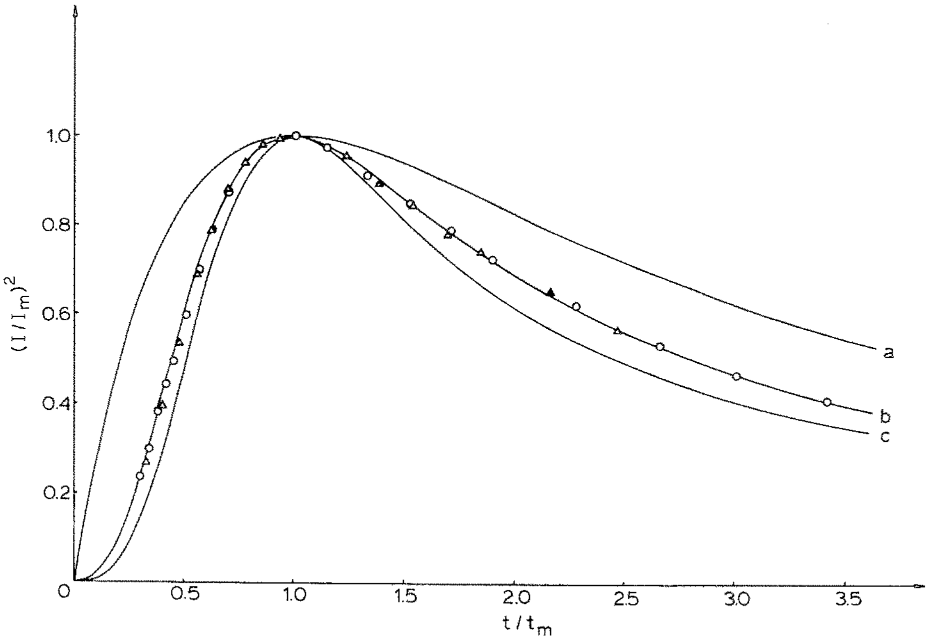

Fig. 6. Non-dimensional plots drawn according to Equation 5 for η_n = 0.270 V. For an explanation of lines a, b and c, see text beneath Equation 6.

5. Discussion and conclusions

The results described in this paper confirm the inhibiting effect of tartaric entities during the growth of electrodeposited silver reported in [1–4, 6]. Concerning the initial, nucleation stage of the process it has been found that $KNaC_4H_4O_6$ does not affect the nucleation rate constant, A, but diminishes the number, N_0, of active sites for nucleation on the electrode surface.

Undoubtedly an important point in any experimental study concerns the reliability of the determined physical quantities. In the very early part of the experimental current transients in Fig. 3 a decreasing current is observed most likely due to charging processes and/or to reduction of platinum oxide at the overpotentials η_n. Apparently such parallel electrochemical reactions may contribute to the original nucleation and growth current of silver clusters thus changing the coordinates (i_m, t_m) of the current maxima. Therefore, values of A and N_0 somewhat higher than the actual ones are likely to be obtained for the particular experimental system. On the other hand according to [7] the nucleation exclusion zones are considered as containing no electroactive species whereas the actual concentration of metal ions around the growing clusters is in fact higher than zero [13]. Although the $A(C_0)$ dependence is not very strong ($A \sim C_0^{1-\beta}$), where β is the transition coefficient [5]) due to this effect, the Scharifker model will predict lower rates of nucleus formation.

Finally a recent paper by Slyuters-Rehbach *et al.* [14] suggests a new definition of the nucleation exclusion zones which leads to a more complicated expression for the current transient and predicts a more intensive process of nucleus formation.

This brief analysis shows that at this stage the theory is far from perfect and therefore one should consider with a certain reservation the results of any theoretical analysis of experimental data. In our opinion one possibility for testing the theory is to carry out parallel experimental measurements of some accessible physical quantity, say the steady state nucleation rate $I_{st} = AN_0$, by means of different experimental methods. The results of such comparative studies recently published [8] seem to favour the relatively simple model developed in [7], which is the reason for its use in the present work.

Another possibility to check the theory is, of course, to compare it with the results from an appropriate simulation experiment.

Acknowledgement

This project was completed with the financial support of the Committee of Science at the Council of Ministers under contract N KH 168 (1987). The main part of the current measurements were carried out by means of scientific equipment donated to A.M. by the Alexander von Humboldt Foundation (FRG).

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